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# **FATE AND TRANSPORT OF AMMONIUM PERCHLORATE IN THE SUBSURFACE**

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**FATE AND TRANSPORT OF AMMONIUM PERCHLORATE IN  
THE SUBSURFACE**

REPORT PREPARED FOR

MELE ASSOCIATES, INC.  
HSC/XRE SUPPORT CONTRACTOR  
BROOKS AFB, TEXAS

PREPARED BY

DR. RAYMOND C. LOEHR  
DR. LYNN E. KATZ  
MR. DANIEL R. OPDYKE

ENVIRONMENTAL AND WATER RESOURCES ENGINEERING PROGRAM  
THE UNIVERSITY OF TEXAS AT AUSTIN  
AUSTIN, TEXAS

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# FATE AND TRANSPORT PARAMETERS FOR AMMONIUM PERCHLORATE IN THE SUBSURFACE

## I. INTRODUCTION

### Objectives and Overview

This report was prepared in response to a Statement of Work (SOW) provided by MELE Associates, Inc., HSC/XRE Support Contractor at Brooks AFB, Texas, Purchase Order No. 0085. The SOW Determination of the Fate and Transport of Ammonium Perchlorate in the Subsurface is being evaluated utilizing a three phase approach. This report addresses the task in the SOW identified as Phase I. Phases II and III will identify and validate the fate and transport of ammonium perchlorate in the subsurface.

The Phase I tasks to be accomplished were identified as:

- a) conduct a literature search of information regarding the fate and transport of ammonium perchlorate in the environment,
- b) based on the information gathered in the literature study, provide recommendations for necessary bench scale studies to validate the information provided.

Implicit in the second task was the need to provide recommendations to fill gaps in knowledge identified from the literature search.

This report was accomplished in the period of February 15 through April 15, 1998 and responds to both tasks. The report was prepared by Dr. Raymond C. Loehr, Dr. Lynn E. Katz and Mr. Daniel R. Opdyke, Environmental and Water Resources Program, The University of Texas at Austin.

### Need for Evaluation

Perchlorate ( $\text{ClO}_4^-$ ) is the oxidation product of chlorate ( $\text{ClO}_3^-$ ). It appears in compounds such as ammonium perchlorate, potassium perchlorate, sodium perchlorate, and perchloric acid. Ammonium perchlorate is highly reactive in its solid state and is used as an oxidizer in many composite propellants used for solid rocket fuel. A typical composite propellant is a mixture of a number of ingredients including a binder, an oxidizer, aluminum powder, a plasticizer, a ballistic modifier, a bonding agent and an antioxidant. The finely ground crystalline ammonium perchlorate oxidizer is embedded in a plastic resinous or rubbery matrix containing these other ingredients. The binders used in this matrix have developed over the years and have ranged from the early use of asphalt, polysulphides and polyesters to the more modern use of polyurethanes and polybutadienes (Bunyan et al., 1993). Polybutadiene acrylonitrile terpolymers (PBAN) cured with epoxides have been used for the space shuttle. The hydroxyterminated polybutadiene (HTPB) prepolymer commonly used in composite propellant productions can form a loosely

crosslinked network when cured with isoporone diisocyanate and will retain its rubbery properties at low temperatures. An example composition of this solid matrix is shown in Table 1.

**Table 1. Composition Of Solid Propellant Used In Space Shuttle (Frosch et al., 1980)**

Ingredient	% by Weight
Ammonium perchlorate	69.60
Al	16.00
Fe <sub>2</sub> O <sub>3</sub>	0.40
PBAN	14.00

In order to improve the adhesion between the oxidizer and the binder, small quantities of bonding agents such as polyamines and aziridines are added to the propellant mix. Antioxidants such as 2,2'methylene-bis(4-methyl-6-tert-butylphenol) are added to reduce the rate at which the polybutadiene reacts with oxygen. Three aging processes have been identified that affect the propellant properties: moisture induced recrystallization of ammonium perchlorate, migration of additives, and oxidative crosslinking of the binder (Bunyan et al., 1993). These processes can lead to hardening of the propellant even in the presence of antioxidants and give rise to limited shelf lives for the propellants.

Because of their limited shelf life, composite propellants containing ammonium perchlorate must be periodically removed from missiles and rockets in inventory and replaced with a fresh supply. Large volumes of the composite propellant have been disposed at sites where this replacement has occurred. Much of this waste material had been burned in open pits and residual propellant and waste were washed from the area to the surrounding soils. Ammonium perchlorate is extremely stable when dissolved in water at concentrations as high as 1,000 mg/L.

Ammonium perchlorate has been found in ground and drinking water, particularly since March 1997, when the California Department of Health Services (CDHS) developed an interim analytical procedure that allows perchlorate concentrations as low as 4 ppb to be reported. Perchlorate has been found in drinking water wells in California, in the outflow of Lake Mead, in groundwater in Las Vegas, in water from a California Superfund site, and in groundwater near certain industrial sites in California.

Perchlorate is not regulated by the U.S. Environmental Protection Agency at this time. However, the 1996 Safe Drinking Water Act (SDWA) requires EPA to compile a list of problematic contaminants that should be scrutinized by EPA over the next decade. On March 2, 1998, EPA finalized its first Contaminant Candidate List (CCL) which includes 60 contaminants. Perchlorate is one of the contaminants on the CCL (USEPA, 1998).

EPA has prioritized this list by developing two categories. The first category includes 20 contaminants which will be evaluated as regulatory candidates. Perchlorate is not among this list of 20 contaminants that will get priority attention. Perchlorate is among the other 40

contaminants for which EPA judges that more research and exposure data is needed before these latter contaminants can be considered for regulation.

California, through the CDHS, has adopted a provisional action level of 18 ppb for perchlorate in drinking water. This apparently resulted from an EPA review of the toxicology of perchlorate which recommended reference dose levels of perchlorate in drinking water of 4-18 ppb.

Past efforts to remove perchlorate from drinking water have focused on ex-situ groundwater treatment techniques and on treatment of wastewater generated from the replacement of missile and rocket propellant.

However, it is also important to understand the fate and transport of perchlorate in both unsaturated and saturated subsurface environments. In order to predict the fate and transport of perchlorate in subsurface systems it is necessary to understand: a) how surface disposal of ammonium perchlorate composite propellants results in perchlorate groundwater contamination, b) how perchlorate dissociates from the composite propellant, c) how perchlorate and the other propellant ingredients migrate through soils, and d) how perchlorate interacts with soil particles as a function of soil and groundwater chemistry. This understanding will: a) allow answers to questions concerning the length of time it will take for perchlorate in the subsurface to reach a receptor, and b) identify in-situ technical approaches that may be effective in controlling and remediating contaminated groundwater.

This report is an initial attempt to acquire pertinent information related to the fate and transport of perchlorate in subsurface unsaturated and saturated soils. Factors that have been assessed include solubility, sorption, biological and chemical degradation, and volatility.

## II. CONCEPTS AND PATHWAYS

The purpose of this section is to briefly provide the context for the fate and transport of perchlorate in the subsurface environment.

### Risk Assessment Paradigm

For chemicals in soils, the basic risk assessment paradigm describes a "path" a contaminant must follow in order to pose a threat. Such a paradigm (Figure 1) can be described as follows. For chemicals to pose a threat to human health and the environment, there must first be a source of contamination. A chemical of concern must then be released from its chemical matrix and may interact with the soil. Once released from the matrix or the soil, transformations may occur that can change the chemical. The chemical, or one of its products, must then be transported to a receptor such as a human, plant, or other object. If the chemical contacts a sensitive area of that receptor, it may cause a negative effect. The risk associated with the chemical in the soil causing a negative impact can be calculated, and this amount of risk may be considered acceptable or unacceptable. In either case, determination of the risk requires an assessment of the hydrodynamic characteristics of the site and the operative reaction processes that will control the fate and transport of the chemical and its products.



**Figure 1. Conceptual Risk Reduction Paradigm**

Somewhat different transformation reactions can occur in saturated and unsaturated soils. Some of the possible reactions that can occur for a generic contaminant are noted in Table 2. The relative impact of each of these possible reactions is often controlled by the physical and chemical characteristics of the contaminant including its solubility, vapor pressure, aqueous density, Henry's constant, diffusivity, and oxidation-reduction potential. Furthermore, the impact of each of these characteristics on the fate and transport of contaminants is dependent on site characteristics such as soil properties, the presence of other aqueous and non-aqueous species and the concentration of the contaminants of interest. For example, the ammonium perchlorate waste from rockets is a mixture that contains metals such as aluminum and the organic binder described earlier. The presence of high concentrations of other metals and the properties and concentrations of the binder are likely to have an effect on the reactions that occur with ammonium perchlorate.

**Table 2. Physical/Chemical Reactions in Soils**

POSSIBLE REACTIONS
<ul style="list-style-type: none"> <li>• biological degradation under aerobic and anoxic conditions</li> <li>• dispersion, diffusion, dilution</li> <li>• volatilization</li> <li>• sorption</li> <li>• chemical reduction or oxidation</li> <li>• photolysis (at the surface)</li> </ul>

### Site Conceptual Model

Different reactions can occur at various locations in the subsurface since the chemical concentrations and environmental conditions at most contaminated sites vary both spatially and temporally. Figure 2 depicts a conceptual model of the spatial variation often observed at

contaminated groundwater sites resulting from spills. One of the main features displayed in this figure is the decrease in concentration of the contaminant between the three regions shown.

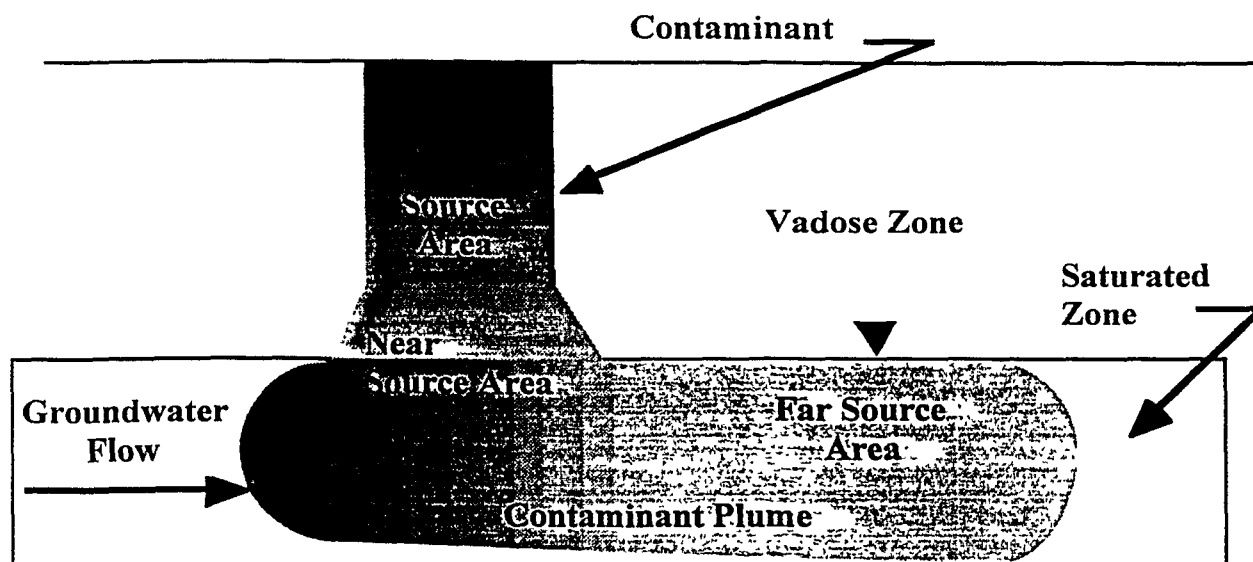


Figure 2. Conceptual Model of Contaminant Transport

#### Source

The highest contaminant concentrations are typically observed near the source of the spill. In the source area, the contaminant is often found as a separate or pure phase in contact with the soil particles. For the case of ammonium perchlorate propellants that have been spilled on the surface and are flushed with water, the extent of dissolution of the ammonium perchlorate in the water will depend on whether the ammonium perchlorate is still associated with the binder and the properties of the binder. Indeed, the tacky nature of most composite propellants can lead to agglomeration of the propellant and poor contact with water (McIntosh, 1969).

If dissolution occurs, water containing the ammonium perchlorate can then percolate through the soil. In addition, rainwater may aid in this process. However, the extent to which the ammonium perchlorate dissociates and percolates through the soil is a function of the amount of water that is applied to the site, the soil composition, and the concentration of perchlorate and other chemicals, such as the binder constituents, in the percolating water.

As rainwater infiltrates the unsaturated zone, water is adsorbed by the soil particles and the contaminants can undergo a number of different reactions. For example, the loss of water to the soil can result in a salting out effect in which a compound such as sodium chloride or ammonium perchlorate precipitates in the unsaturated zone due to a decrease in the water content.

Sorption and degradation processes may also be prevalent. In surface soils, one expects higher amounts of organic matter, microorganisms and chemically reactive sites. Generally, aerobic conditions are present. However, as ammonium perchlorate dissociates, it is likely that the ammonia will be utilized by nitrifying organisms that are ubiquitous in soils, particularly surface soils. This will result in the formation of nitrate and the utilization of oxygen in the soil gas in



the unsaturated zone. In turn, the source area will become anoxic. In addition, the degradation of the organic binder material can place an oxygen demand that also contributes to anoxic conditions. In addition, degradation of the binder may be required before the ammonium perchlorate is mobile.

The contaminants can also interact directly with the soils. Hence, the soil characteristics also affect the transport of chemicals through a soil. For example, organic content, specific surface area, cation exchange capacity, and anion exchange capacity are all parameters that have been shown to have an effect on the extent of sorption for particular contaminants. The relative importance of each of these parameters on sorption is dependent on the characteristics of the chemical of concern, the properties of other chemicals in the source area and the soil properties.

### Near Source

All of the above processes will reduce the concentration of ammonium perchlorate in the aqueous phase as it migrates downgradient. Thus, in the near source area it is likely that high ammonium perchlorate concentrations will persist, however, the contaminant is less likely to be present in the pure phase and the relative concentrations of ammonium and perchlorate will likely change due to biodegradation processes that consume oxygen. Since the oxygen, organic matter and carbon concentrations decrease with depth in the unsaturated zone, the operative reaction phenomena will likely change as the contaminants migrate through the unsaturated zone and into the saturated zone.

Reactions that occur in the saturated zone in the near source area will be controlled by the soil and solution characteristics. The contaminant concentrations will still be relatively high, however, anoxic conditions may or may not prevail depending on the source of the groundwater flow.

The soil organic matter content is likely to be lower in the near source area. Chemicals which have a lower organic carbon partition coefficient ( $K_{oc}$ ) will partition less strongly to soil containing lower amounts of organic carbon. These contaminants will be more mobile in the near source area compared to the source area. As a result, for a given transport distance, a decrease in the extent of retardation provides less time for chemical and biological reactions.

Clay soils and soils in the deeper horizon generally have lower organic contents but may have high cation exchange capacities depending on the clay mineralogy. These minerals contain a net negative surface charge due to isomorphic substitution. As a result, cationic chemicals such as  $Ca^{++}$  and  $Sr^{++}$  will undergo ion exchange reactions with these minerals and will be retarded relative to the groundwater. In general, negatively charged chemicals will not sorb to these fixed charge sites.

However, clay minerals and oxide phases such as iron and aluminum oxides also contain variable charge sites that result from the interaction of surface oxygen atoms with water to form surface hydroxyl groups (Figure 3). These surface hydroxyl groups are considered to react like diprotic acids in which a site can be either negatively charged, neutral or positively charged depending on the pH as shown in Figure 3. At low pH, oxide minerals have a net positive surface charge because the surface contains more  $SOH^{2+}$  groups than  $SO^-$  groups. If the pH is increased to the

point where the number of  $\text{SOH}^{2+}$  groups is equal to the number of  $\text{SO}^-$  groups, then the surface is neutral. This pH is referred to as point of zero charge ( $\text{pH}_{\text{pzc}}$ ). Below the  $\text{pH}_{\text{pzc}}$  the surface is positively charged and above the  $\text{pH}_{\text{pzc}}$  the surface is negatively charged. Values of the  $\text{pH}_{\text{pzc}}$  for a variety of minerals are presented in Table 3. Sorption of cations and anions to these variable charged sites will be highly pH dependent.

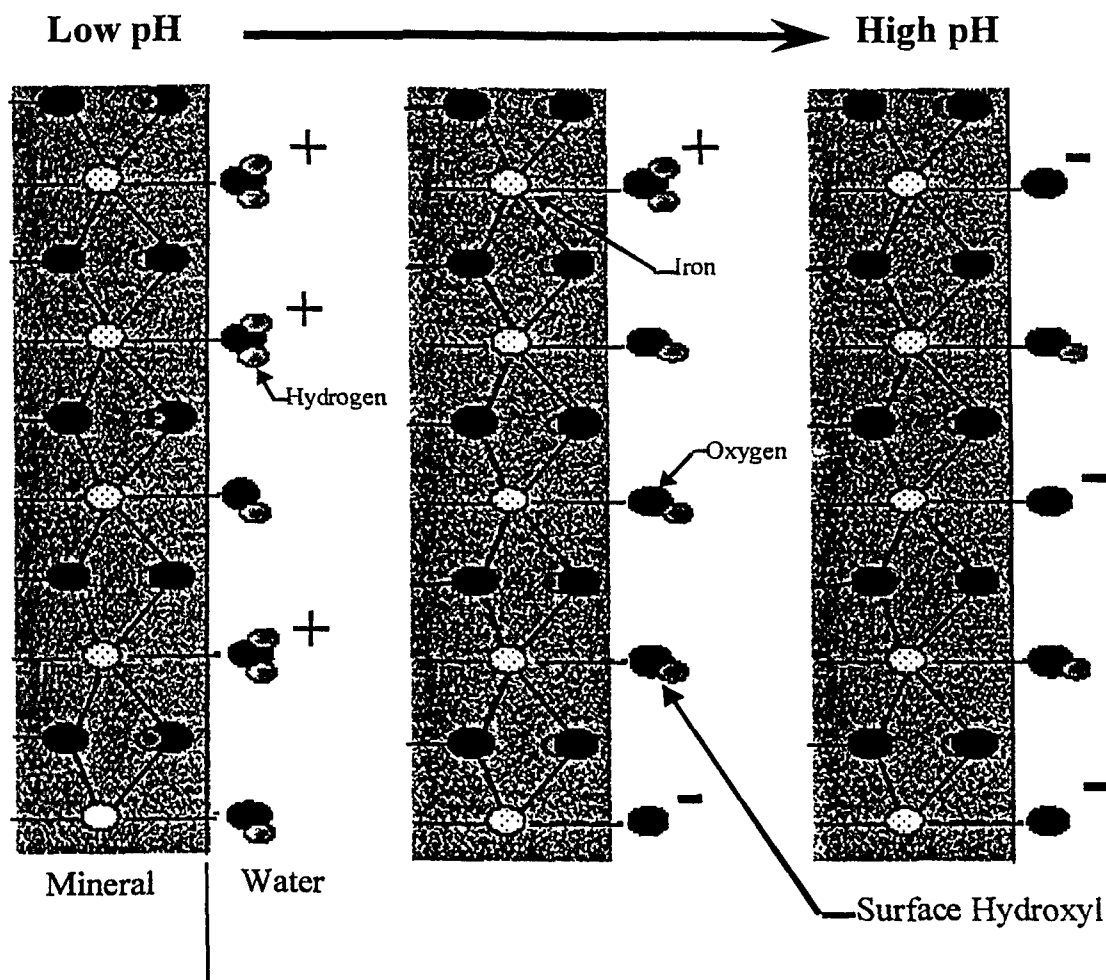


Figure 3. Effect of pH on Variable Charge Mineral Surfaces

Thus, the pH of a soil solution can affect the fate and transport of a chemical in the subsurface. Western soils tend to be alkaline with high concentrations of calcium, magnesium and possibly iron. Eastern U.S. soils tend to be acidic with high aluminum concentrations. Since pH affects both sorption and the speciation of many chemicals in the subsurface, it is important to consider the effect of pH and the predominant local ions when considering the chemical and biological transformation of potential contaminants in the subsurface.

The characteristics of a soil are also important with respect to other surface reactions such as oxidation and reduction. Mineral surfaces such as manganese oxides have been shown to

facilitate oxidation of a number of contaminants such as Cr(III) (Fendorf and Zasoki, 1992; Oscarson et al., 1983).

Table 3. Point of Zero Charge ( $\text{pH}_{\text{pzc}}$ ) of Minerals

Material	$\text{pH}_{\text{pzc}}$
$\alpha\text{-Al}_2\text{O}_3$	9.1
$\alpha\text{-Al}(\text{OH})_3$	5.0
$\alpha\text{-FeOOH}$	7.8
$\text{Fe}(\text{OH})_3$ (amorphous)	8.5
$\text{SiO}_2$	2.0
Kaolinite	4.6
Montmorillonite	4.6

From Stumm and Morgan (1981)

Inorganic and organic constituents in a soil solution also impact the extent of sorption in a system. These constituents can affect the pH and speciation of contaminants through acid/base, complexation, precipitation and oxidation/reduction reactions.

#### Far Source

All of the processes described above are also dependent on the absolute and/or relative concentration of the contaminants. The contaminant concentration in the saturated zone will decrease with distance from the source due to attenuation processes that include physicochemical and biological reactions and hydrodynamic dispersion processes. As shown in Figure 2, the aqueous phase concentrations of perchlorate are expected to be relatively dilute and fewer opportunities for chemical and biological reactions are possible as the contaminant migrates from the near sources area to the far source area. This decrease in contaminant concentration can have a dramatic effect on the mobility of the contaminant in the far source area.

Concomitant changes in the soil/solution environment are also expected to influence the fate and transport of a contaminant as it migrates from the source area to the far source area. As a result, evaluation of the fate and transport of contaminants resulting from spill events must examine the processes that will affect contaminant mobility and degradation in each of the areas shown in Figure 2. It should be recognized however that the conceptual model presented in Figure 2 is very simplistic since it implies the possibility of homogeneous conditions in the subsurface. In reality, subsurface soils are very heterogeneous which affects the transformations and transport of ammonium perchlorate and other chemicals.

### Fate and Transport Aspects

Thus as indicated above, to understand the fate and transport of chemicals that enter the soil it is necessary to: a) identify the most relevant factors that may affect a particular chemical in each region, and b) characterize the site specific factors that can be used to predict the likely movement of a chemical in each region. The complexities indicated above clearly indicate that any fate and transport modeling that might be done to estimate perchlorate movement at a site should account for: a) the heterogeneities of the site subsurface conditions; b) the spatial and temporal variation in concentrations likely to occur in the source area, near source area, and far source area; and, c) the varying physical, chemical, and biological conditions that exist in the unsaturated and saturated soils.

Such information also is relevant to determining site specific approaches to remediating unsaturated and saturated soils containing a chemical of concern. Possible approaches include: a) in-situ systems such as reactive walls (funnel and gate), biological degradation, chemical reduction, bioventing, and air sparging, b) ex-situ systems for groundwater treatment before use or discharge such as ion exchange, reverse osmosis, and granular activated carbon filtration, or c) a combination of in-situ and ex-situ options. Decisions on which system(s) is most appropriate should be made on a site specific basis.

The intent of this report is to identify the parameters that affect the transformations and transport of perchlorate in subsurface soils under conditions such as in Figure 2 so that site-specific fate and transport modeling as well as contaminant management and remediation decisions can be made.

### III. TRANSFORMATION AND TRANSPORT PARAMETERS FOR AMMONIUM PERCHLORATE

#### Data Sources

Many sources of information were consulted to obtain the information in the following sections. The sources that provided the most relevant information are cited in this report.

#### Solute Properties.

Table 4 presents a list of the physical and chemical properties of ammonium perchlorate that are expected to control the fate and transport of perchlorate ion in the environment or impact the efficacy of various treatment processes. The table contains the parameter value for each property, the relevant conditions under which it was measured and the source of the data. A brief summary of the significance of each of these properties is provided in the following sub-sections to identify the physical, chemical and biological processes that warrant further consideration.

#### Solubility

The solubility of a contaminant can have a dramatic effect on the rate of migration in groundwater systems. Compounds with a low solubility have the potential to precipitate out of the aqueous phase thereby retarding their migration. As shown in Table 4, the aqueous solubility

of ammonium perchlorate is 20.2 g/100g solution @25°C as reported by Greenwood and Earnshaw (1984). This value indicates that dissolution of solid ammonium perchlorate is expected and that the negatively charged perchlorate ion will predominate in solution especially in locations far from the source.

**TABLE 4**  
**TRANSFORMATION AND TRANSPORT PARAMETERS FOR AMMONIUM PERCHLORATE**

Parameter	Value	Source
Molecular Weight	117.49 g/mole	
Solubility	20.2 g/100g solution @25°C	Greenwood and Earnshaw, 1984
Standard Potential		
$\text{ClO}_4^- + 2\text{H}^+ + 2\text{e}^- = \text{ClO}_3^- + \text{H}_2\text{O}$	1.201 @25°C/1.19	Dean 1992
$\text{ClO}_3^- + 2\text{H}^+ + \text{e}^- = \text{ClO}_2 + \text{H}_2\text{O}$	1.175/1.15	Charlot et al. as
$\text{ClO}_2 + \text{H}^+ + \text{e}^- = \text{HClO}_2$	1.188/ 1.27	referenced in Horányi
$\text{HClO}_2 + 2\text{H}^+ + 2\text{e}^- = \text{HClO} + \text{H}_2\text{O}$	1.64/ 1.64	and Bakos 1992
$2\text{HClO} + 2\text{H}^+ + 2\text{e}^- = \text{Cl}_2 + 2\text{H}_2\text{O}$	not given/ 1.63	
$\text{Cl}_2 + 2\text{e}^- = 2\text{Cl}^-$	1.396/ 1.36	
Overall Reaction:		* as calculated from half-reactions
$\text{ClO}_4^- + 8\text{H}^+ + 8\text{e}^- = 4\text{H}_2\text{O} + \text{Cl}^-$	1.388/ 1.38*	
Vapor Pressure	Non-Volatile	
Density	1.95 g/cm <sup>3</sup> at 20°C	CRC (1988)

The solubility of ammonium perchlorate is temperature dependent according to the following relationship as shown by Hiquily and Laguerie (1982).

$$S = 9.924 + 0.5745 \cdot T + 0.001123 \cdot T^2$$

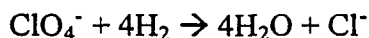
where S is the solubility in g/100g H<sub>2</sub>O and T is the temperature in °C. This equation indicates that, even at freezing temperatures, the solubility of ammonium perchlorate is 9.9g/100gH<sub>2</sub>O which is orders of magnitude higher than the CDHS provisional action level of 18 ppb.

The solubility of other salts containing perchlorate was also examined to evaluate the potential for precipitation of perchlorate ion due to the presence of other ions (the common ion effect). Aqueous solubility of perchlorates decreases in the following order: Na>Li>NH<sub>4</sub>>K>Rb>Cs (Greenwood and Earnshaw, 1984). For example, KClO<sub>4</sub> has a solubility of 1.99 g/100 g H<sub>2</sub>O at 20°C (Greenwood and Earnshaw, 1984) which is approximately one-tenth of the solubility of ammonium perchlorate. As a result, if solid ammonium perchlorate dissolves in the presence of potassium, some of the perchlorate ion could re-precipitate as potassium perchlorate. The potential for perchlorate re-precipitation in the subsurface will depend on the temperature of the system, the potassium ion concentration and the perchlorate concentration. Thus, the likelihood of perchlorate precipitation will vary as the contaminant migrates downgradient since the concentrations of perchlorate are expected to decrease due to attenuation processes.

#### Standard Potential

The standard potential provides an indication of the oxidation/reduction potential of a compound. The values represent the electromotive force of a cell in which hydrogen is oxidized at a standard hydrogen electrode (P<sub>H<sub>2</sub></sub> = 1 atm), reduction occurs for the compound of interest at the connecting electrode, and all species are present at unit activity. Positive values of the standard electrode potential indicate that the reaction will proceed spontaneously when the activities of all species in solution are unity. Negative values indicate that the reverse reaction will proceed spontaneously.

The standard electrode potentials for the sequential reduction of perchlorate ion at a +7 oxidation state to chloride ion (oxidation state = -1) are shown in Table 4. The standard potential is positive in all cases, which indicates that reduction is thermodynamically favorable. Indeed, the standard redox potential of the ClO<sub>4</sub><sup>-</sup>/Cl<sup>-</sup> system is 1.36 V, therefore, it is thermodynamically possible to reduce ClO<sub>4</sub><sup>-</sup> ions by hydrogen under atmospheric pressure at room temperature (Horányi and Vértes, 1974) according to the following reaction:



The data for perchlorate reduction also indicates that reduction should be enhanced at lower potentials such as those found in anaerobic or anoxic systems. As discussed previously, in subsurface soils, the oxygen concentration is expected to decrease as a function of distance from the source due to biodegradation processes. The formation of anoxic and anaerobic regions should favor the reduction of perchlorate from a thermodynamic perspective.

While the value of the electrode potential indicates that the reaction is thermodynamically feasible, there is very little evidence in the literature suggesting that the reaction occurs spontaneously. Vértes and Horányi (1974) have provided evidence for the reduction of perchlorate to chloride, however, temperatures ranged from 40°C to 90°C and a tungsten carbide catalyst was required. The rate of this reaction has been shown to depend on hydrogen partial pressure, the concentration of ClO<sub>4</sub><sup>-</sup> ions, the hydrogen ion concentration and temperature and

required the presence of the tungsten carbide catalyst (Horányi and Vértes, 1974). The results also indicate that the rate of reduction is negligible at room temperature. Thermodynamically, the reduction of  $\text{ClO}_4^-$  ions on any electrode would be expected at potentials below 1.0 V/RHE (Bakos and Horányi as referenced in Wasberg and Horányi 1995).

These results suggest that the reduction of perchlorate may be kinetically limited under ambient conditions in the absence of chemical or biological catalysts. The findings are consistent with a number of statements indicating that perchlorate is the most stable oxo-compounds of chlorine (Greenwood and Earnshaw, 1984) and its common use as a non-reactive supporting electrolyte in geochemical and environmental studies.

The kinetic stability of perchlorate ion has been attributed to the fact that perchlorate has no low-lying unfilled electronic orbitals that could accommodate an additional electron to form  $\text{ClO}_4^{2-}$  ion. Therefore, the reaction must occur via an O atom transfer as shown in Table 4. However, oxygen transfer requires another species to stabilize the oxygen such as protons and certain metals.

#### Vapor Pressure

The vapor pressure of a substance provides an indication of its potential for partitioning to the gas phase. The higher the equilibrium vapor pressure at a given temperature, the more volatile the compound. No values for the vapor pressure ammonium perchlorate could be found in the literature. However, values for ammonium chloride should be of similar magnitude and were reported in a number of handbooks. The vapor pressure of ammonium chloride ranged from 1 torr at 160.4°C to 760 torr at 337.8°C. At 25°C, the vapor pressure would be considerably less than 1 torr. In comparison, the temperature required to reach a vapor pressure of 1 torr for sodium chloride is 865°C. Thus, ammonium salts are more volatile than sodium salts. Nevertheless, volatilization is not considered to be a predominant pathway at ambient temperatures.

#### Density

The density of solid ammonium perchlorate is 1.95 g/cm<sup>3</sup> at 20°C. This value indicates that the solid material is more dense than water at the same temperature. Hence, the solid will sink in water. Concentrated solutions of ammonium perchlorate are also more dense than water (Zaytsev and Aseyev, 1992).

#### Attenuation Processes

The discussion of the solute properties presented above indicates that there are several potential attenuation processes that may affect migration of perchlorate in subsurface systems. These processes include precipitation, biological or chemical reduction, and adsorption and ion exchange. Each of these processes will act to a different extent and at different rates depending on the site-specific environmental conditions, the relative concentration of perchlorate, and the effect of the binder chemicals. In particular, the rates and extent of these processes will vary as the contaminant migrates from the source area to the far source area. The following discussion

provides an evaluation of the relative importance of these processes in the source, near source and far source regions. Most of the background literature that addresses perchlorate reactions was derived from research examining treatment of ammonium perchlorate waste. To the extent possible, this literature provides the basis for the hypotheses generated in this section.

### Source Area

Typical characteristics of the source region shown in Figure 2 include high concentrations of ammonium perchlorate, possibly high concentrations of the binder, and relatively high organic content soils. The fate and transport of perchlorate in this area is highly dependent on the composition of the overall propellant. For example, degradation of the binder can lead to direct interactions between ammonium perchlorate and the soil environment. Aerobic biodegradation of ammonium perchlorate, sorption, precipitation and organic complexation may be possible. Chemical reduction of perchlorate is not likely due to kinetic limitations and the presence of an oxidizing environment. It should also be noted, however, that oxygen limitations may result in this region if the extent of aerobic degradation is significant enough to deplete the oxygen content. Under these circumstances, anoxic biodegradation may occur, although, chemical reduction is still unlikely.

#### *a) Dissolution*

If ammonium perchlorate was initially deposited at the surface in a complex mixture containing the binder and bonding agents contained in the propellant, release of the ammonium perchlorate crystals from the binder would be required prior to transport. Indeed, MacIntosh (1969) states, "although many oxidizers used in propellants are soluble in water, the oxidizer contained in fragments of solid propellant discarded as waste cannot be dissolved out of the propellant merely by placing said fragments in water." Presumably, propellant waste containing ammonium perchlorate that has been washed from the site has already undergone size reduction so that ammonium perchlorate crystals are exposed. Slow release of the ammonium perchlorate solid from this mixture could represent a long term source of contamination. Indeed, there have been a number of efforts to improve processes for separating ammonium perchlorate from these mixtures and these studies have shown that a high degree of mixing, increased temperatures and/or addition of surface active agents (surfactants) are required to prevent the agglomeration of ammonium perchlorate crystals by adsorbing onto the propellant binder surfaces (Shiu et al., 1995).

#### *b) Complexation and Precipitation*

The extent of precipitation of a solid phase is controlled by the solubility of the phase, the temperature of the system, and the presence of common ions or complexing agents. For example, the high solubility value for ammonium perchlorate and its temperature dependence indicate that stoichiometric precipitation of ammonium perchlorate in distilled water will lead to aqueous concentrations of perchlorate of greater than 180,000 ppm at 20°C. Depending on the total mass of perchlorate residing in the system and the rate of degradation of ammonium in the system due to nitrification, solid ammonium perchlorate could precipitate in the unsaturated zone and represent a long term contaminant source.



As indicated earlier, a number of other cations such as potassium form salts that are much less soluble than ammonium perchlorate. For example, potassium perchlorate is approximately one order of magnitude less soluble than ammonium perchlorate. Therefore, the presence of  $K^+$  ions could lead to precipitation of potassium perchlorate. Indeed, the relatively low solubility of  $KClO_4$  has been used to treat concentrated ammonium perchlorate wastestreams. In this process, the waste stream containing perchlorate is concentrated and ammonia and volatile organics are stripped from the water at high temperatures (150-240°F). Potassium hydroxide or potassium chloride is then added to the hot concentrated solution to form  $KClO_4$ . Since the solubility of the perchlorate salts is temperature dependent, the solution is cooled to achieve crystallization. Mower (1995) reported that the best results were obtained when the temperature was below 40°F. In this patented process, KCl was added to waste streams containing 100,000-250,000 ppm of perchlorate and effluent concentrations containing less than 6,000 ppm were achieved. (Mower, 1995). Thus, reprecipitation of perchlorate with other cations in the system is possible especially if ammonium exchanges with other cations adsorbed to the soil. If reprecipitation occurs, the solid potassium perchlorate could redissolve over time resulting in long term dissolution of perchlorate to infiltrating surface water.

Since perchlorate is not a strong ligand, the potential for natural complexing agents to interfere with the precipitation process is unlikely. However, a number of synthetic organics have been shown to interact with perchlorate to form insoluble complexes. Kopchinski and Meloan (1996) describe the selective precipitation of dichromate and perchlorate from an aqueous solution using an organic compound. In this laboratory study, *N*-4-Vinylbenzyl-*N'*-1,4-diazabicyclo[2.2.2]octane was synthesized and added to an aqueous solution of 51 anions at a concentration of 0.1M each. Perchlorate and eight other anions (dichromate, ferricyanide, nitro ferricyanide, persulfate, picrate, dithionate, tetrafluoroborate, and iodide) precipitated out. The other forty-two anions did not. The initial concentrations of the anions in these solutions was 0.1M which is much lower than the potential concentrations at the near source region.

### c) *Aerobic Biodegradation*

Aerobic biodegradation of the propellant is possible in this region, particularly for the ammonium contained in the system. A number of microorganisms are capable of reducing ammonia to nitrite (e.g. *Nitrosomonas*) and nitrite to nitrate (e.g. *Nitrobacter*) in aerobic environments. This process is referred to as nitrification and utilizes 4.57 mg of oxygen per mg of ammonia as N. The literature search conducted as part of this study did not identify any evidence for aerobic biodegradation of perchlorate.

### Near Source Area

In the near source area, the concentration of perchlorate is expected to be lower than in the source area. In addition, it is likely that in the unsaturated near source area the oxygen content of infiltrating water has been reduced due to biodegradative processes in the source area. The oxygen concentration of waters in the saturated zone of the near source area may be either aerobic or anoxic depending on the source and characteristics of the recharge water and the operative reaction processes that have occurred in the aquifer upgradient of the waste site. For

the purposes of this discussion, anoxic conditions are presumed such that the potential transformation or retardation processes for perchlorate include chemical reduction, anaerobic degradation and sorption.

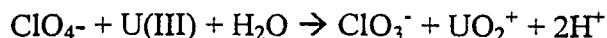
*a) Chemical Reduction*

The redox potential for water in an aerobic environment ( $pO_2 = 0.21$ ) is 800 mV at neutral pH. The redox potential for anaerobic conditions can go as low as -400mV. Under these conditions the chemical reduction of perchlorate ion is thermodynamically feasible as indicated by the standard potential reported in Table 4. In most cases the process is kinetically hindered due to the electronic structure of the ion. For example, research evaluating the use of iron, enhanced iron (NiFe), and iron sulfide for treating water containing an average perchlorate concentration of 7,300 ug/L did not show any perchlorate reduction even though the process is thermodynamically feasible (EnviroMetal Technologies Inc., 1997). Similar results with respect to a lack of perchlorate reduction were found with sulfide compounds (Catts, 1998).

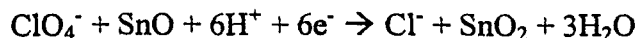
While these studies indicate that chemical reduction is not a feasible remediation option, there are a number of studies outside of the environmental literature that do indicate that perchlorate can be reduced either homogeneously or heterogeneously under controlled conditions and in the presence of substances which can stabilize oxygen during perchlorate reduction. The homogeneous reduction of perchlorate has been observed in the presence of V(III), Ti(III) and U(III) species at ambient temperatures (Taube, 1982). The reduction reactions in these cases are:



and



In addition, perchlorate has undergone reduction in acidic solutions at the surface of electrodes made of platinum, tungsten carbide, ruthenium, carbon impregnated with chromate and aluminum oxide, aluminum and titanium (Horányi and Bakos, 1994). The results of these studies indicate that the main product of reduction in these systems is  $Cl^-$  ion. In the majority of these studies, hydrogen was assumed to promote the perchlorate reduction. However, studies by Painot and Augustynski (1975), Almeida et al. (1997) and Brown (1986) suggested that the reduction occurs by a direct reaction at the surface in which adsorbed perchlorate is reduced and a surface species is oxidized. For example, Almeida et al. (1997) have proposed the following reaction for reduction of perchlorate on oxidized tin:



and Painot and Augustynski (1975) proposed a similar reaction for reduction in the presence of aluminum which is present in ammonium perchlorate waste streams. The perchlorate reduction appears to be a function of pH, applied potential and the presence of oxide on the electrode surface (Almeida et al., 1997). It also appears that other anions such as  $Cl^-$  and  $SO_4^{2-}$  retard the

reduction process on metal electrodes via a competitive adsorption process (Brown, 1986). As a result, the process may be inhibited by adsorbed  $\text{Cl}^-$  species derived from the reduction process (Wasburg and Horányi, 1995).

The results of these studies with electrodes indicate that perchlorate reduction can be achieved at metal surfaces under acidic pH if the potential of the system can be controlled, if inhibition of the process can be avoided, and if there are no other competing anions in the system at significant concentrations.

#### b) Biodegradation

Although the reduction of perchlorate is thermodynamically possible, it is rarely observed due to very slow kinetics. This slow rate of reduction is due to the high activation energy for this reaction. However, this activation energy may be overcome by certain microorganisms, resulting in an energy yield for those microorganisms. Four groups of researchers have investigated the reduction of perchlorate by microorganisms. Their observations are summarized in Table 5 and discussed below.

One of the first reported applications of biological treatment of perchlorate containing wastewaters is presented by Yakovlev et al. (1971). In this patent, the authors describe a process of mixing water containing inorganic oxygen containing compounds (such as perchlorate) or hexavalent chromium with municipal sewage in an anaerobic tank. Under anaerobic conditions, the biochemical oxidation of organic matter is linked to the biochemical reduction of the inorganic oxygen-containing compounds or hexavalent chromium. This process uses the naturally occurring consortium of micro-organisms commonly found in municipal sludge. After anaerobic treatment, excess BOD was treated by standard aerobic biochemical methods. For the entire system, influent ammonium perchlorate concentrations ranged from 142 to 424 mg/L, and effluent (treated) concentrations were on the order of 3 mg/L. Hydraulic residence time in the unaerated tank ranged from 4.5 to 9 hours. Attaway and Smith (1994) report the volumetric reaction rate of this process to be approximately 12 mg  $\text{ClO}_4^-$  per hour per liter.

In 1976, Korenkov et al. described a similar process of mixing industrial wastewaters containing perchlorates with municipal sludge in an anaerobic tank. However, in this patent, the rate of perchlorate reduction is increased by the presence of a strain of the micro-organism *Vibrio dechloraticans* Cuznesove B-1168. This micro-organism is strictly anaerobic and grows well in the presence of perchlorate and any of several carbon sources, including acetate and ethanol. It can also reduce chlorate and small amounts of nitrate. For this process, influent concentrations of ammonium perchlorate were 600 mg/L. This water was then diluted to 100 mg/L with municipal waste waters. This combined waste stream was then treated anaerobically; "during this time the perchlorate-ion is completely reduced to chlorides" (Korenkov et al. 1976). Under the conditions described in the patent, the rate of reduction of perchlorate is as high as 70 mg/g of biomass solids per hour (Korenkov et al. 1976). Attaway and Smith (1994) list this rate as over 100 mg/hour per liter. This rate is reported to be an increase of "5-10 times as compared to the prior

Table 5. Summary of Biodegradation of Perchlorate

Source	Micro-organism	Conditions	Electron Acceptors	Carbon/Nutrient Source	Effluent Conc. of $\text{ClO}_4^-$	Rates (mg $\text{ClO}_4^-$ /hr/L)
Yakovlev et al. 1971	Municipal sludge consortium	Anaerobic	Perchlorate, Hexavalent chromium	Sludge	3 mg/L	12
Korenkov et al. 1976	Municipal sludge consortium and <i>Vibrio dechloraticans</i> Cuznesove B-1168	Anaerobic	Perchlorate, Chlorate, Nitrate	Sludge, Acetate	BDL	>100
Attaway and Smith 1994; Hurley et al. 1996	Municipal sludge consortium and <i>Wolinella succinogenes</i> HAP-1	Anaerobic	Perchlorate, Chlorate, Nitrate	Brewer's Yeast	BDL of 0.5 ppm	221
Rikken et al. 1996	Strain GR-1 of the B subgroup of Proteobacteria	Anaerobic	Perchlorate, Chlorate, Oxygen, Nitrate, Mn(IV)	Acetate	Unknown	Unknown

art process", where "the prior art process" appears to be the patent by Yakovlev et al. (1971) described above (Korenkov et al. 1976).

Attaway and Smith, 1994 described another process for the biodegradation of perchlorate under anaerobic conditions. As described in the patent, the following components are combined in an anaerobic reactor:

1. Perchlorate containing industrial waste waters
2. An aqueous stream containing *Wolinella succinogenes* HAP-1 and a consortium of facultative anaerobic.
3. An organic slurry containing high protein organic nutrients such as aged brewer's yeast, cottonseed protein, or whey powder.

The *Wolinella succinogenes* HAP-1 micro-organism is strictly anaerobic and capable of reducing perchlorate, chlorate, and nitrate (but not nitrite). The reactor is maintained at pH 7.0 to 8.5 and 32-37°C. The growth of the consortium on the organic slurry removes oxygen, nitrate, nitrite, sulfate, and sulfite, generates hydrogen, and maintains the low redox potential ( $< -300$  mV) required for optimum perchlorate reduction. After the perchlorate is reduced, an aerobic reactor is used to remove any remaining oxygen demanding material. Advantages of this system over previous systems include a) an increased rate of perchlorate degradation, b) a tolerance for high perchlorate concentrations, and c) a self-contained nutrient feed system that does not require municipal sludge. In their example, the influent concentration of ammonium perchlorate was 15,000 ppm. This was diluted to yield an approximate concentration of 3,000 ppm, which was then input to the anaerobic reactor. Effluent from the system was less than 10 ppm. The specific degradation rate of the HAP-1 micro-organism is at "least 1,492 mg  $\text{ClO}_4^-$ /hr per gram of dry biomass, a 21-fold increase over previous methods" (Attaway and Smith 1994). On a volumetric basis, this is at least twice as high as previous methods (221 mg  $\text{ClO}_4^-$ /hr liter vs. 100 mg  $\text{ClO}_4^-$ /hr liter). The cited previous methods appear to be the work of Korenkov (1976).

The Armstrong Laboratory Environics Directorate has developed a pilot-scale biodegradation reactor at Tyndall AFB, Florida (Hurley et al., 1996) based on the patent of Attaway and Smith (1994). This pilot scale system operates with a residence time as low as 8 hours, using Brewer's yeast as the nutrient source, a pH between 7.0 and 7.35, and a temperature of 40°C. Ammonium perchlorate concentrations were reduced from 3,000 ppm to below the detection limit of 0.5 ppm.

Rikken et al. (1996) describe another micro-organism that can reduce perchlorate. This bacteria, strain GR-1 of the B subgroup of Proteobacteria, was grown on acetate and perchlorate. As opposed to the micro-organisms described above, this bacteria is facultatively anaerobic and can use oxygen, nitrate, Mn(IV), perchlorate, and chlorate as electron acceptors but cannot use sulfate, iodate, bromate, chlorite, selenate, or Fe(III). It can grow on acetate, propionate, capryonate, malate, succinate, and lactate. Perchlorate reduction only occurs in the absence of molecular oxygen. The reduction of perchlorate to chlorite generates energy for cell growth. The chlorite then disproportionates to molecular oxygen and chloride without generating energy that can be used by the bacteria. The bacteria then reduces the oxygen to water, thereby maintaining bulk anaerobic conditions. In this way, the GR-1 bacteria can reduce perchlorate to chloride without the assistance of a facultatively anaerobic consortium (to remove the oxygen) as is required by the *Wolinella succinogenes* HAP-1 and *Vibrio dechloraticans* Cuznesove B-1168 micro-organisms described above.

The literature described above indicates that there are a number of generalizations that can be made regarding biodegradation of perchlorate in the near source area:

1. Reduction of perchlorate is frequently proportional to release of chloride; this indicates complete reduction of perchlorate.
2. The accumulation of intermediates has not been observed.

3. Reduction of perchlorate increases biomass. Experimental evidence indicates that micro-organisms can use the energy released from the reduction of perchlorate to chlorite, but not from chlorite to chloride (the last step).
4. The reduction of perchlorate only occurs under anaerobic conditions. Some micro-organisms that can reduce perchlorate are strictly anaerobic (*Wolinella succinogenes* HAP-1 and *Vibrio dechloraticans* Cuznesove B-1168) and at least one is facultatively anaerobic (strain GR-1 of the B subgroup of Proteobacteria).
5. Some specific micro-organisms appear to reduce perchlorate at higher rates than the consortium of micro-organisms in municipal sludge.

### c) Sorption

The data presented previously indicate that perchlorate is typically present in water as an anion and it is generally considered to be stable with respect to its reactivity. The extent of adsorption of anions to surfaces is highly dependent on the characteristics of the surface including its surface charge and surface area. In general, perchlorate is expected to sorb more weakly than  $\text{Cl}^-$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HSO}_4^-$  or  $\text{NO}_3^-$  to a variety of positively charged surfaces including metal electrode surfaces. For example, onto platinum, the order of sorption preference is generally assumed to be:  $\text{Cl}^- > \text{H}_2\text{PO}_4^- > \text{HSO}_4^- > \text{ClO}_4^-$  (Horányi and Inzelt, 1978). Similarly, on gold electrodes the order of adsorption strength was reported to be  $\text{Cl}^- > \text{HSO}_4^- > \text{OH}^- > \text{ClO}_4^-$ . In other studies examining reduction at metal electrodes, sulfate and chloride were shown to inhibit perchlorate adsorption presumably due to the inability of perchlorate to compete for adsorption sites on the electrode surface (Horányi and Bakos, 1994).

Adsorption of perchlorate to variable charge soils that carry both negatively and positively charged surface sites, depending on the pH of the system, follows adsorption trends that are similar to those found on metal electrodes. In a study examining the effect of salt solutions containing perchlorate, nitrate and chloride on sulfate adsorption, Zhang et al. (1996) found that sulfate adsorption was pH and anion dependent with sulfate adsorbing to a greater extent at low pH where the surface carries a greater positive surface charge. In general at low pH, sulfate adsorption decreased with increasing salt concentration for all of the anions. However, at higher pH there was an increase in adsorption with increasing salt concentration for nitrate and perchlorate but not for chloride. The trends observed for nitrate and perchlorate are commonly found for adsorption of anions in electrolyte solutions. The results for chloride suggest that chloride interacts more specifically with mineral surfaces than either nitrate or perchlorate. Indeed, comparison of the effect of the different anions on sulfate adsorption reveals that the relative adsorption strength for the three anions is  $\text{Cl}^- > \text{NO}_3^- > \text{ClO}_4^-$ .

In studies examining adsorption of chloride, nitrate and perchlorate by variable charge soils, Liang and Ling (1992) and the iron oxyhydroxide mineral goethite (Maneepong and Wada, 1991) it was also concluded that the extent of adsorption followed the same order:  $\text{Cl}^- > \text{NO}_3^- > \text{ClO}_4^-$ . Sorption to the soils in the former study also showed the typical decrease in sorption with increasing pH that is typical for anions. This study also showed that the order of addition of the anions in bi-solute experiments did not affect the trends observed. This suggests that the sorption

of these anions is reversible. Finally, this study also showed that the addition of an iron oxide coating on the soils led to an increase in adsorption of the anions because the iron oxide surface carries a greater positive surface charge due to its relatively high point of zero charge (Table 1).

#### Far Source Area

In the far source area, the concentration of perchlorate is expected to be significantly lower due to hydrodynamic dispersion and any other attenuation processes that may have occurred in the near source area. The oxygen concentration is expected to be lower than in the near source area, hence, anaerobic biodegradation and/or chemical reduction may be operative in this region. However, as stated earlier there is little evidence that would support the chemical reduction of perchlorate in these systems. Thus, sorption and anaerobic biodegradation are the most likely processes to affect the fate and transport of perchlorate in this system.

##### *a) Sorption*

As indicated above, perchlorate sorbs very weakly to most soil minerals. The extent of sorption in this region compared to the near source area will depend on the differences between the soil mineralogy and solution characteristics such as pH and ionic strength. However, in both cases the extent of perchlorate sorption is expected to be small.

##### *b) Biodegradation*

All of the biodegradation studies described for the near source area were conducted at high initial perchlorate concentrations. These concentrations could be significantly higher than the concentrations expected in the far source area and therefore the extent of biodegradation may be very different in this region. Korenkov et al. (1976) claim complete reduction of perchlorate. However, it is unlikely that all of the perchlorate was reduced. Rather, any remaining perchlorate was probably below their detection limit, which was not reported. Due to the dramatically lower detection limits possible with today's technology, it is possible that their effluent concentrations were higher than the concentration in the far source groundwater considered by this report (130 ppb). Therefore, it is unclear whether or not this process could be successfully applied to water containing perchlorate in the hundreds of ppb range.

Very few studies have addressed biodegradation of perchlorate at low concentrations. Researchers at The University of California at Riverside have isolated a bacteria that is capable of reducing aqueous solutions of 45  $\mu\text{g ClO}_4^-/\text{l}$  and 130  $\mu\text{g ClO}_4^-/\text{l}$  to chloride, with residual perchlorate concentrations at below the detection limit (Frankenberger, 1998). However, these results have not yet been published.

#### IV. INTERPRETATIVE EVALUATION

The discussion in the previous section makes it possible to identify processes listed in Table 2 that should be considered for evaluation in determining the fate and transport in each of the regions identified in Figure 2. Certain processes can be ruled out based on the values of the parameters provided in Table 4. For example, volatilization and chemical oxidation can be ruled out based on values of vapor pressure and oxidation/reduction potential.

A significant process that will affect the fate and transport of perchlorate in the source area is the extent to which the ammonium perchlorate is still associated with the binder. Processes that allow bound ammonium perchlorate to be released from bulk mixtures or exposed to the surface/water interface will facilitate ammonium perchlorate dissolution, degradation and transport.

In the source area, aerobic biodegradation of ammonium and possibly the binder may occur. No evidence for aerobic degradation of perchlorate was found in the literature. Dissolution and precipitation processes could be important in this region due to the potentially high concentrations of ammonium perchlorate and limited amount of water in the unsaturated zone. The extent of dissolution and reprecipitation processes will be highly dependent on the soil composition, infiltration rate and the concentrations of anions and cations in the soil solutions. Studies should be conducted with actual field soils containing ammonium perchlorate to evaluate these processes.

In many contaminant transport scenarios, sorption has a major impact on the mobility of contaminants in the near source and far source areas. However, for perchlorate, all of the data indicate that sorption to mineral soils will be minimal and that perchlorate will not compete favorably for sorption sites compared to other weakly sorbing anions such as nitrate and chloride. Chemical reduction is a possible transformation process in anoxic or anaerobic zones, however, there have not been any studies that have indicated that chemical reduction will occur under the environmental conditions expected in the subsurface. Anaerobic biodegradation in the near source area does appear to have potential based on the fact that a number of different organisms have been shown to degrade high concentrations of perchlorate. However, there has been no evidence for field-scale biodegradation reported in the literature.

Dispersion processes are likely to have the most significant effect on the concentrations of perchlorate in the groundwater in the far source area. Biodegradation may occur based on the evidence provided by Frankenberger (1998) that a bacterial isolate can degrade low concentrations of perchlorate, but no field data is available to support this laboratory study.

## **V. VALIDATION OF AVAILABLE INFORMATION**

An important conclusion from this review is that the processes occurring in the source area will have a significant impact on the mobility of perchlorate in the subsurface. To develop a fate and transport model to describe the migration of perchlorate, it is essential to obtain a better understanding of the precipitation/dissolution processes that occur in the source area and in other areas where the concentration of perchlorate is high enough for precipitation and other processes to dominate. The type of Phase II information required to elucidate the mechanisms controlling these processes include:

- characterization of soil properties, such as mineralogy, anion and cation exchange capacity, sorption characteristics, organic content; this should be done for soils at sites where the composite propellant has been disposed of to the soil,
- determination of the composition of ammonium perchlorate mixtures or complexes,



- characterization of the hydrology of the site,
- characterization of the infiltrating groundwater at the site, and
- characterization of leachates produced from source and near source soils collected from the site.

There are also a number of evaluative studies that should be conducted to identify the likelihood of possible transformation and transport reactions that could occur in the subsurface. Recommendations are:

A. Since the role of the binders and other propellant ingredients is so unclear with respect to their effect on ammonium perchlorate transformations and transport, particularly in the source and near source zones, an evaluation of the following is warranted.

- 1) The extent to which the binder and other chemicals are present in the contaminated soil at the source and near source areas should be ascertained.

Chemical analyses should be conducted for soils obtained from ammonium perchlorate propellant waste sites that have been identified as a source of perchlorate contamination. These analyses should include quantitative and qualitative analyses to determine the identity of soil contaminants and their concentrations.

- 2) The extent to which the binder chemicals can be degraded in the source and near source areas should be determined.

Aerobic and anaerobic treatability studies should be conducted using samples of the composite propellants disposed of at relevant sites. These studies should consist of basic Tier I biological treatability studies in which slurry microcosms are seeded with surface soil and activated sludge from the treatment of industrial wastewater. Parameters evaluated should be oxygen depletion, carbon dioxide production, nitrate generation and reduction, pH and Microtox relative toxicity. For anaerobic treatability studies, methane generation also should be determined. Different propellant to reactor mixture ratios should be used to identify the effect of propellant concentration on the treatability results.

- 3) The leachability of ammonium perchlorate from the composite propellant should be identified.

Samples of the composite propellant should be subjected to slurry equilibrium and column leaching studies. For comparability and consistency, the EPA Synthetic Precipitation Leaching Procedure (SPLP) fluid should be used. In addition, leaching studies should be conducted using synthetic water that mimics the characteristics of infiltrating rainwater at a selected site. In both cases, the leachate should be analyzed for ammonia, perchlorate, pH, Microtox relative toxicity, UV/Visible spectroscopy and TOC as a surrogate measure of the organics in the propellant waste and their degradation products. The leachate also could be analyzed for metals and for more detailed chemical identification using mass spectrometry.

- B. The role of chemical reduction of ammonium perchlorate, particularly in the presence of metals and metal salts, such as those found in the composite propellant (Al) and in soils (Fe, Al) should be evaluated because of their favorable thermodynamics. Although previous studies have not provided evidence for chemical reduction, these studies have not been conducted in environments representative of waste disposal sites. The resultant information will be useful to better understand what happens to ammonium perchlorate, particularly in the source and near source zones.

Different quantities of the composite propellant can be mixed with organic surface soils and mineral subsurface soils. The different quantities would allow the effect of concentration to be determined. Slurry equilibrium leaching studies could be conducted. Differing concentrations of dissolved metals would be added to the slurry studies. The leachate would be monitored for ammonium, perchlorate, chloride concentrations, oxidation-reduction potential, pH, as well as for TOC and UV/Visible absorbance.

- C. The interaction of ammonium perchlorate and subsurface soils should be determined to identify the extent that retardation occurs in typical soils. Results of these studies will be useful to understand the extent to which ammonium perchlorate is transported in the near and far source zones.

Samples of subsurface soils near locations where the perchlorate is known to be in groundwater should be obtained. Subsurface soils from other locations, particularly not in the arid west, should be obtained to provide a comparison. These soils should be characterized for organic matter, type (sand, silt, clay), particle size, cation exchange capacity (CEC), anion exchange capacity (AEC), and pH.

The soils should be packed in vertical columns, dilute concentrations of ammonium perchlorate added to the top of the columns, and the leachate monitored for perchlorate, ammonia, chloride, TOC and UV/Visible absorbance. In essence, a series of routine chemical retardation experiments should be conducted. Abiotic conditions should be assured and a recognized tracer, such as tritium, added so as to have a marker against which perchlorate retardation can be determined.

In summary, information about the characteristics of typical sites and the results of the above evaluations will permit a better understanding of the fate and transport of ammonium perchlorate at locations where waste composite propellant is allowed to enter the soil. As indicated, the specific information and results will more clearly indicate what is likely to happen to ammonium perchlorate in the source, near source and far source areas of a site.

The results that will be obtained from the recommended Phase II evaluations can be used to better understand and predict migration of perchlorate in the subsurface, both conceptually and as part of a mathematical groundwater model.

## VI. CONCLUSIONS/SUMMARY

A review of literature addressing the fate of ammonium perchlorate was presented in the context of a conceptual model describing perchlorate transport in a scenario in which ammonium perchlorate propellant waste is disposed at the soil surface and is leached into the subsurface. This conceptual model can be used to describe the fate and transport of ammonium perchlorate as a function of distance from the source area and changes in the biogeochemical environment. Environmental factors of critical importance include the redox potential (e.g. aerobic or anaerobic), the concentration of the contaminant and other constituents of the propellant, the soil characteristics, and the hydrology of the site.

The conceptual model indicated how these factors are expected to affect the reactions that occur as the contaminant moves from high concentrations in the source area, to lower concentrations in the near source area and finally to regions in the underlying aquifer that are far downgradient from the source. Dissolution and precipitation reactions are presumed to have the most significant effect on perchlorate migration in the source area and anaerobic biodegradation and infiltration rates are expected to have more of an impact as the contaminant migrates to the aquifer. Once the contaminant reaches the aquifer, hydrodynamic dispersion and anaerobic biodegradation are expected to have the most significant impact on perchlorate attenuation. The effects of sorption are expected to be minimal, and the potential for chemical reduction remains questionable.

This information was then used to indicate potential studies that would address the questions raised regarding the composition of the waste at the source and the significance of the processes identified above for retarding the migration of perchlorate. The Phase II research proposed included waste characterization, site characterization, biodegradation, leachability and chemical reduction treatability studies. These Phase II studies are expected to fill many of the gaps in the current understanding of perchlorate biogeochemistry and to develop fate and transport models to describe perchlorate migration in the subsurface.

## VII. ACKNOWLEDGMENTS

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